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Transient Absorption Probe of Intermolecular Triplet Excimer of Naphthalene in Fluid Solutions: Identification of the Species Based on Comparison to the Intramolecular Triplet Excimers of Covalently-Linked Dimers

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We report here the observation of the laser-induced transient absorption spectrum of intermolecular triplet excimers of naphthalene in fluid solution. This assignment is confirmed by comparison to the transient absorption spectra of the intramolecular triplet excimers of covalently linked dimers of naphthalene and quinoxaline.

Introduction

As the lowest energy excitation trap, triplet excimers of aromatic molecules are important species for understanding the excitation energy transport in chemical and biological systems. Most of the past studies on triplet excimers have been based on time-resolved emission measurements in fluid solutions.[1] However, because of the difficulty of distinguishing the weak excimer emissions (phosphorescence and delayed fluorescence) from emissions of strongly emitting impurities, it has proven problematic in some cases to identify and characterize triplet excimers by emission measurements. The most notable example is the intermolecular triplet excimer of naphthalene, about which there has been lively debate.[2−4] Absorption spectroscopy is the method of choice for studying triplet excimers, but in order for it to be a general technique the electronic absorption of the triplet excimer must be strong and distinctly different from the absorption due to the triplet monomer. Theoretical considerations[5−7] of the excimer absorption for naphthalene suggest that a strongly allowed intermoiety charge transfer (CT) transition of the excimer (triplet[6,7] as well as singlet[5]) occurs at wavelengths substantially longer than the $T_n \leftarrow T_1$ triplet−triplet and $S_n \leftarrow S_1$ singlet−singlet absorptions of the monomer. Such transitions have in fact been observed for various triplet excimers of covalently linked aromatic molecules, including naphthalene.[8] In this paper, we report the observation of a laser-induced transient absorption spectra of the intermolecular triplet excimer of naphthalene whose assignment is confirmed by comparison to the covalently linked dimers of naphthalene and quinoxaline.

Experimental Section

Time-resolved absorption spectra were measured using two different laser photolysis systems. The first system, utilizing an excimer laser and an intensified diode array (Excimer /PDA), has been described in detail.[9] The second system, to be referred to as the YAG/ICCD system, uses a Nd:YAG laser (Spectra-Physics GCR-150), and an intensified CCD (ORIEL INSTASPEC V) and a photomultiplier (Hamamatsu 1P28) for the multichannel detection of the transient absorption and temporal measurements, respectively. Single-shot triggering is accomplished for both detectors by a pulse generator that triggers a home-built black box that receives constant TTL signals from the laser flashlamps. The black box in turn triggers a mechanical shutter placed between an Oriel 150 W Xe−Hg high-pressure arc lamp and the sample chamber, as well as the Q-switch on the laser. The Q-switch is used to trigger either a Tektronix TDS-640a oscilloscope (for time-resolved measurements) or a SRS DG-535 pulse generator (for triggering the ICCD detector). Data acquisition and analysis on the time-resolved system is accomplished using Lab View (data acquisition) and Igor Pro (data analysis). Data acquisition is accomplished for the ICCD using the Oriel software.

The detection of intermolecular triplet excimers by transient absorption requires relatively high concentration of the ground-state (S_0) species. In highly concentrated solutions, however, the light absorption by the sample is confined to thin layers of the solution very close to the sample cell wall, and thus it is difficult to make measurements of the transient absorption of the electronically excited species. For the probe of intermolecular triplet excimers of naphthalene, we have therefore utilized an indirect excitation method first used by Ohno and Kato.[10] In this approach, the lowest triplet (T_1) of naphthalene is produced by sensitized energy transfer from T_1 benzophenone, formed by photoexcitation of S_0 benzophenone at wavelengths (e.g., 355 nm) not absorbed by S_0 naphthalene. The T_1 naphthalene formed by the triplet−triplet energy transfer then associates with S_0 naphthalene, to produce an intermolecular triplet excimer. The method allows the formation of evenly distributed triplet excimers in concentrated solutions of naphthalene, that can be detected by time-resolved absorption in a 1 cm cuvette. The advantage of using benzophenone in the triplet sensitization of naphthalene is that the transient absorption spectrum of triplet benzophenone as well as that of the ketyl radical are well characterized, and there is no evidence for the formation of a complex or an exciplex between benzophenone and naphthalene. Experiments of Shizuka and co-workers[11] on triplet sensitization of naphthalenophanes demonstrate that the ketyl radical ($\lambda_{obs} = 545$ nm) is not produced even under high-power (40 mJ/pulse) excitation of benzophenone by the third harmonic (355 nm) of a Nd:YAG laser. In our experiments,

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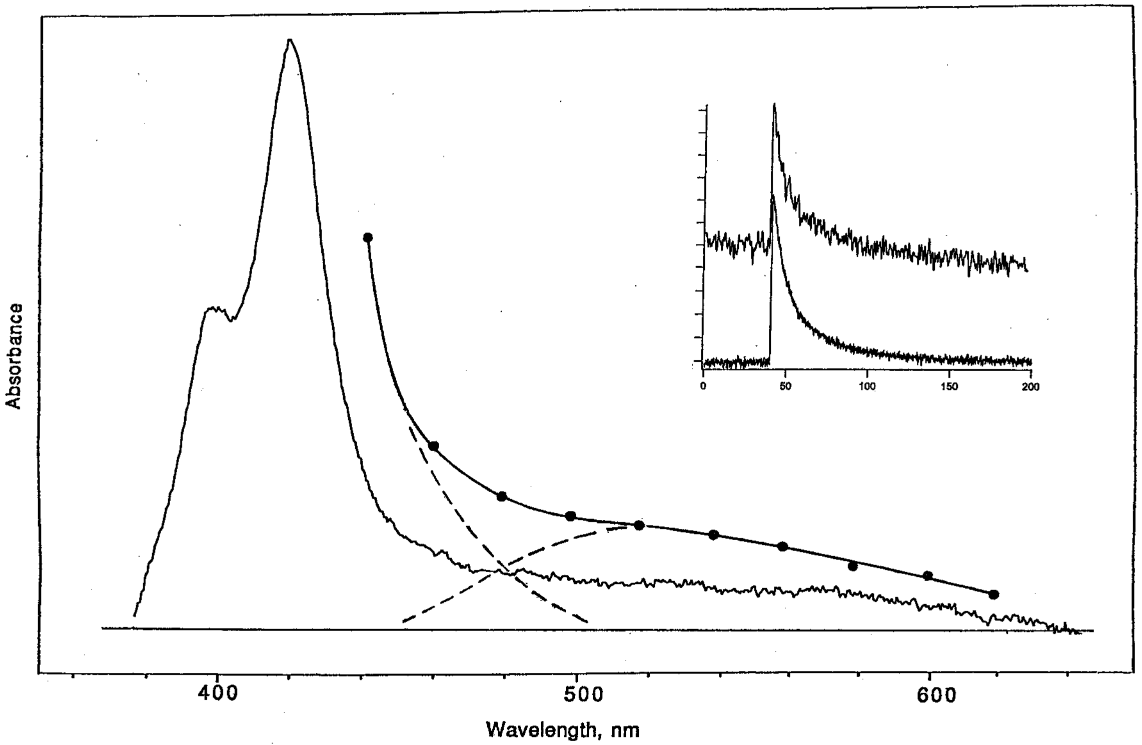

Figure 1. Benzophenone-sensitized transient absorption spectrum of a 3 M solution of naphthalene in toluene at room temperature. The spectra were recorded with the YAG/ICCD system (see Experimental Section) with $\lambda_{exc} = 355$ nm, delay = 1.5 μs, and gate width = 1.0 μs. The sharp feature with intensity maximum at about 420 nm is the well-known absorption spectrum of the triplet monomer, whereas the broad feature with intensity maximum at about 520 nm is assigned to the intermoiety charge-transfer (CT) absorption band of the intermolecular triplet excimer. The curve with solid circles represents the wavelength-by-wavelength measurements of the absorption with a photomultiplier (see text). The insert shows the temporal characteristics of the monomer absorption at 440 nm and the excimer absorption at 530 nm (upper trace). The time scale is in μs.

approximately 10^{-2} M of benzophenone in 1−4 M solutions of naphthalene were excited with about 25 mJ/pulse of the 355 nm Nd:YAG laser beam.

Scintillation-grade naphthalene from Fischer was used without further purification. GC/MS analysis of the sample showed no impurity of any kind, which places the purity of the naphthalene sample at greater than 99.98%. The quinoxaline-annelated dimer (dimethyl-11-oxodimethyl-quinoxalino-[2,3-*c*]dimethylquinoxalino[2′,3′-*h*]-bicyclo[4.4.1]undecane-1,6-dicarboxylate], and the corresponding quinoxaline-annelated monomer (dimethyl-3-oxo-1,2,4,5-tetrahydroquinoxalino[2,3-*d*]-cycloheptene-2,4-dicarboxylate) were synthesized and purified following the procedure of Mataka et al.[13] The semirigid naphthalene dimers, 7,14-endoxy-7H,14H-cycloocta[1,2,3-*de*:5,6,7-*d′e′*] dinaphthalen-7-ol (hereafter referred to as the endoxy dimer) was synthesized and purified as described by Agosta.[14] The naphthalene end-labeled poly(ethylene glycol),[15] N−P_5−N, and dinaphtho[*c*,*h*]bicyclo-[4.4.1]undeca-3,8-dien-11-one ethylene acetal[13] were obtained from Professors C.-H. Tung and Shuntaro Mataka, respectively. Solvents of the highest purity from various sources were used as received. The degassing of the solutions was made in a 1 × 1 cm cuvette either by a freeze−pump−thaw technique or by bubbling of Ar gas.

Results and Discussion

Figure 1 presents the benzophenone-sensitized transient absorption spectrum of 3 M solution of naphthalene in toluene at room temperature. While the dilute solution of naphthalene exhibits only the characteristic triplet−triplet absorption spectrum of naphthalene monomer at about 420 nm, the concentrated solution of naphthalene containing benzophenone exhibits, in addition, a weaker absorption extending to about 650 nm. Because of the weakness of the longer-wavelength absorption, the transient absorption spectrum in the region of 450−620 nm can be more accurately recorded by measuring the initial absorbance of the time-resolved absorption as a function of wavelength using a photomultiplier. The spectrum so obtained, shown in Figure 1, is in good qualitative agreement with that obtained from the multichannel detection using CCD. Interestingly, the longer-wavelength absorption (with intensity maximum at about 520 nm) is very similar to the transient absorption spectra of the intramolecular triplet excimers of 1,1-di-α-naphthylmethane[12] and 1,2-dinaphthylethane,[12] and to the visible transient absorption spectrum of neat 1-methylnaphthalene (Figure 2) attributed to triplet excimer.[10] In view of this correspondence and the similarity of the absorption to the transient absorption spectra of naphthalene-annelated dimers that exhibit excimer phosphorescence (vide infra), we assign the 450−650 nm visible band to the intermolecular triplet excimer of naphthalene. This assignment is supported by the observation that the temporal characteristic of the visible band is identical to that of the 380−440 nm absorption of the triplet monomer. The identity of the temporal characteristics of the monomer and excimer absorptions, shown in the inset of Figure 1, demonstrates the rapid equilibration that occur between the triplet monomer and triplet excimer of naphthalene. Consistent with the efficient triplet−triplet annihilation expected in concentrated fluid solutions, the temporal characteristic of the triplet decay is nonexponential. More specifically, the rapid bimolecular decay at early times is followed by a slower unimolecular decay at later times. As expected from the work on naphthalenophanes,[11] the benzophenone-sensitized transient absorption of naphthalene solutions exhibits no spectral feature due to the ketyl radical.

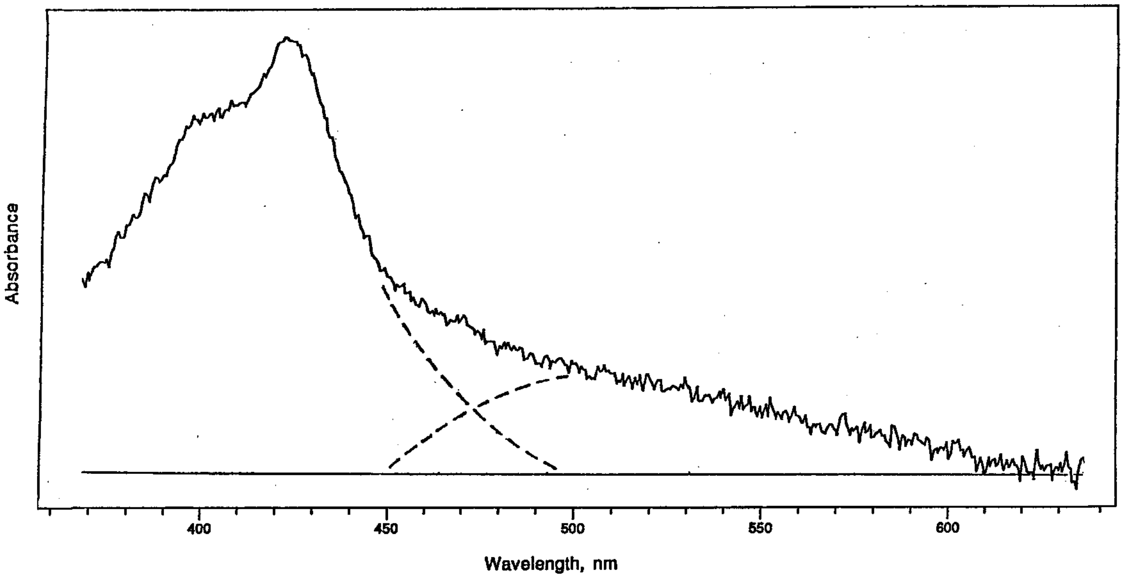

Figure 2. The benzophenone-sensitized transient absorption spectrum of neat 1-methylnaphthalene, measured by the YAG/ICCD system with $\lambda_{exc} = 355$ nm, delay = 1 μs, and gate width = 1 μs.

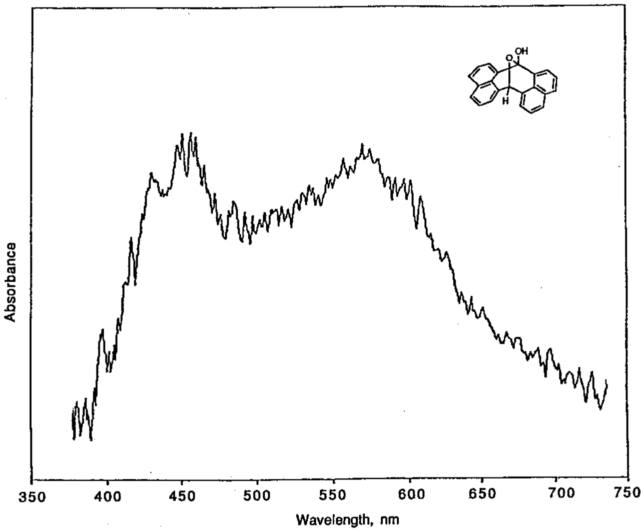

Figure 3. Transient absorption spectrum of a 10^{-4} M solution of the endoxy dimer of naphthalene in acetonitrile at room temperature. The spectrum was recorded with the EXCIMER/PDA system (see Experimental Section) with $\lambda_{exc} = 308$ nm, delay = 5 μs, gate width = 10 μs. The shorter wavelength feature at about 450 nm is due to the triplet−triplet absorption of the locally excited (LE) state, whereas the longer wavelength feature at about 570 nm is the intermoiety CT absorption of the intramolecular triplet excimer.

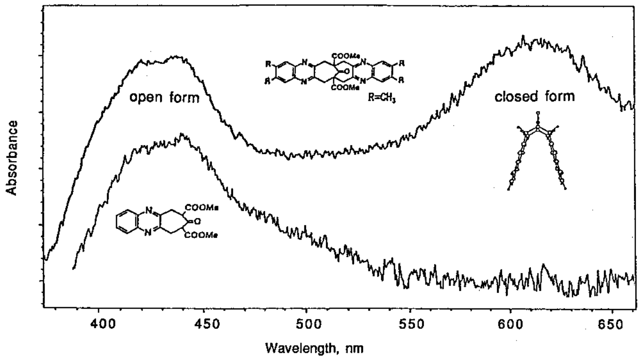

Figure 4. Comparison of the transient absorption spectrum of 10^{-4} M solution of the quinoxaline-annelated dimer (top) with that of the 10^{-4} M solution of the monomer (bottom), in ethanol at room temperature. Both spectra were measured using the YAG/ICCD system with $\lambda_{exc} = 355$ nm, delay = 10 μs, and gate width = 1.0 μs. The shorter wavelength feature at about 425 nm in the upper spectrum is due to the open form[20] of the dimer, whereas the longer wavelength feature at about 610 nm is due to the closed form[20] of the dimer.

In the notation of Chandra and Lim,[16] the triplet−triplet absorption of the naphthalene excimer in the 450−650 nm region corresponds to the intermoiety $^3\delta \leftarrow {}^3\sigma$ charge-transfer (CT) transition from the lowest-energy exciton resonance state ($^3\sigma$) to the lowest-energy charge resonance state ($^3\delta$). This visible absorption of the triplet excimer occurs at the higher energy side of the absorption spectrum of the naphthalene singlet excimer (about 700 nm),[17] which has been assigned[5] to the highly allowed ($f \cong 0.33$) $^1B_{2u}$ ($^1\delta$) $\leftarrow$ $^1B_{3g}$ ($^1\sigma$) CT transition. The large CT character of the $^1B_{2u}$ ($^1\delta$) excimer state of naphthalene is supported by the observation that the transition energy of the $^1\delta \leftarrow {}^1\sigma$ absorption, as well as the visible and near-IR absorptions of other aromatic singlet excimers, scale approximately with the I − A (ionization potential minus electron affinity) of the compound.[18] The higher energy of the intermoiety CT absorption band of the triplet excimer in naphthalene relative to the singlet excimer is reasonable since the singlet and triplet CT states ($^1\delta$ and $^3\delta$) are expected to be nearly degenerate[16] and the lowest-energy excimer triplet state ($^3\sigma$) lies lower than the lowest-energy excimer singlet state ($^1\sigma$).

The assignment of the 520 nm transient absorption in naphthalene and 1-methylnaphthalene to the intermolecular triplet excimer is strongly supported by the observation that similar absorptions occur in all covalently linked dimers of naphthalene and quinoxaline that exhibit excimer phosphorescence.[19] Four such examples are shown in Figures 3−6. Figure 3 shows the transient absorption spectrum of a dilute solution of the L-shaped endoxy dimer of naphthalene in acetonitrile at room temperature. The shorter wavelength feature at about 450 nm is due to the triplet−triplet absorption of the locally excited (LE) state, perturbed by the pendant naphthalene, whereas the longer wavelength feature at about 570 nm is the intermoiety CT absorption of the intramolecular triplet excimer.[6] In Figure 4, we present the transient absorption spectrum of a dilute solution of the quinoxaline-annelated dimer[20] and that of the corresponding monomer in ethanol at room temperature. Comparison of the two spectra reveals that the 425 nm absorption in the dimer spectrum is due to the open form,

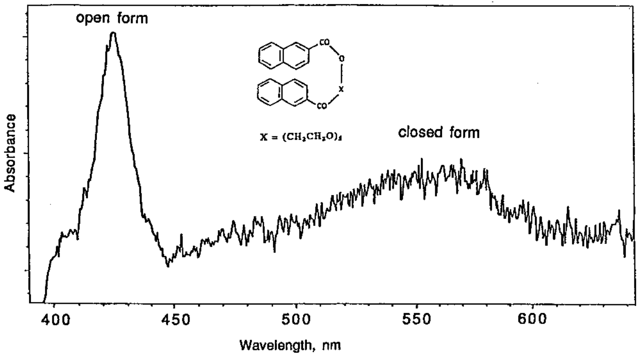

Figure 5. Transient absorption spectrum of 2 × 10^{-4} M solution of the naphthalene end-labeled ethylene glycol in ethanol at room temperature, measured with the YAG/ICCD system. The experimental conditions were λ_{exc} = 266 nm, delay = 5 μs, gate width = 1 μs.

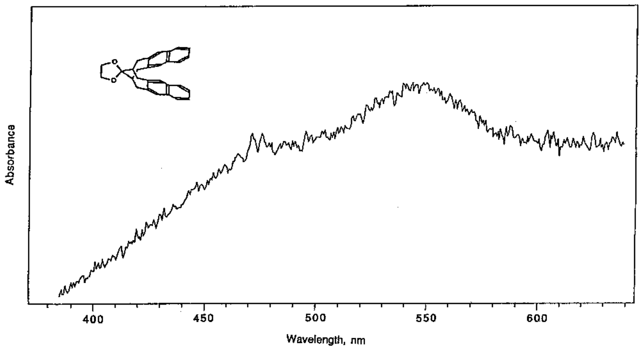

Figure 6. Transient absorption spectrum of a 1 × 10^{-4} M solution of dinaphtho[*c*,*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one ethylene acetal in ethyl acetate, measured with the YAG/ICCD system. The experimental conditions were λ_{exc} = 266 nm, delay = 10 μs, gate width = 1 μs.

whereas the longer wavelength feature at about 610 nm is due to the closed form of a sandwich structure.[20] The triplet excimer resulting from this dimer has also been characterized by both EPR[20] and low-temperature emission measurements.[20] Figure 5 displays the transient absorption spectrum of the naphthalene end-labeled ethylene glycol[15] in ethanol at room temperature. As in the case of the quinoxaline-annelated dimer, we can assign the shorter wavelength feature at about 425 nm to the open form, and the longer wavelength feature at about 560 nm to the closed form of the dimeric species. Finally, in Figure 6, we present the triplet−triplet absorption spectra of dinaphtho[*c*,*h*]bicyclo-[4.4.1]undeaca-3,8-dien-11-one ethylene acetal,[20] which is structurally very similar to the closed form of the quinoxaline-annelated dimer. The shorter wavelength feature at about 470 nm is due to the absorption of the LE triplet state, whereas the longer wavelength feature at about 540 nm is due to the intermoiety CT absorption of the folded dimer.

Where comparisons can be made, the temporal characteristics of the intermoiety CT absorption is identical to that of the corresponding excimer phosphorescence. Thus, the decay rate of the absorption and that of the excimer phosphorescence are essentially identical for both the endoxy dimer of naphthalene and the naphthalene end-labeled poly(ethylene glycol). Similarly, the transient absorption band of the quinoxaline-annelated dimer at ∼ 610 nm decays at the same rate as the excimer phosphorescence of the compound in rigid glass at 77 K (the phosphorescence of the quinoxaline dimer is too weak to be observed in fluid solutions at room temperature[21]). The assignments of the visible absorption bands in the 500−650 nm region to the intramolecular triplet excimers are therefore compelling based on these results.

As previously mentioned, the absorption wavelengths of excimers scale with the I − A values. Thus, whereas the ionization potential of quinoxaline (9.01 eV)[22] is substantially greater than that of naphthalene (8.14 eV),[22] the correspondingly larger electron affinity of quinoxaline (0.71 eV)[21] relative to that of naphthalene (−0.91 eV)[22] renders very similar I − A values for the two compounds (8.30 eV for quinoxaline and 8.33 eV for naphthalene). The similarity of the spectral positions of the triplet excimer absorptions in quinoxaline- and naphthalene-annelated dimers is therefore consistent with their assignments to the intermoiety CT transitions.

In conclusion, the benzophenone-sensitized, transient absorption spectra of concentrated solutions of naphthalene and 1-methylnaphthalene display an absorption at about 520 nm which is similar to the transient absorption spectra of dilute solutions of covalently linked dimers of naphthalene, especially 1,1-di-α-naphthylmethane and 1,2-di-α-naphthylethane. This observation, together with the theoretical considerations, indicates that the visible absorption system is due to the intermoiety CT transition from the lowest energy intermolecular triplet excimer of naphthalene, which is predicted to occur on the higher energy side of the corresponding singlet excimer absorption at about 700 nm. This long-wavelength intermoiety CT transition is useful as a diagnostic tool for the presence of triplet excimers, and is shown to occur in all naphthalene- and quinoxaline-annelated dimers exhibiting excimer phosphorescence.

In future studies, we will explore the dependence of the transition energies of the intermoiety CT absorptions of the triplet excimers on the redox potentials for a series of aromatic molecules. We will also carry out two-color pump−probe studies of ion-pair formation in polar solvents, in which the first laser produces an excimer (singlet or triplet) and the second laser (of different color) induces the transition to the CT state of the excimer.

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Note Added in Proof. Through an oversight, a statement has been left out in the text that the benzophenone-sensitized transient absorption spectrum of naphthalene is also very similar to that of the copolymer COPOP77N, containing 77% naphthalene and 23% benzophenone chromophore (Flamigini, L.; Camaioni, N.; Bortolus, P.; Minto, F.; Gleria, M. *J. Phys. Chem.* **1991**, *95*, 971).

References and Notes

(1) See, for a recent summary, Wang, X.; Tian, J.; Kofron, W. G.; Lim, E. C. *J. Phys. Chem.* **1999**, *103*, 1560.

(2) (a) Nickel, B.; Rodoriguez Prieto, M. F. *Z. Phys. Chem. N. F.* **1986**, *150*, 31. (b) Nickel, B.; Rodoriguez Prieto, M. F. *Chem. Phys. Lett.* **1988**, *146*, 125.

(3) (a) Locke, R. J.; Lim, E. C. *Chem. Phys. Lett.* **1987**, *138*, 489. (b) Locke, R. J.; Lim, E. C. *Chem. Phys. Lett.* **1989**, *160*, 96.

(4) Hüttmann, G.; Staerk, J. *J. Phys. Chem.* **1991**, *95*, 4951.

(5) Sadygov, R.; Lim, E. C. *Chem. Phys. Lett.* **1994**, *225*, 441.

(6) East, A.; Lim, E. C. To be published.

(7) Ishikawa, S.; Nakamura, J.; Iwata, S.; Sunitami, M.; Nagakura, S.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1346.

(8) Modiano, S. H.; Dresner, J.; Lim, E. C. *J. Phys. Chem.* **1993**, *97*, 3480.

(9) Modiano, S. H.; Dresner, J.; Lim, E. C. *J. Phys. Chem*. **1991**, *95*, 9144.

(10) Ohno, T.; Kato, S. *Chem. Lett*. **1976**, 263.

(11) Yamaji, M.; Shima, K.; Nishimura, J.; Shizuka,. *J. Chem. Soc., Faraday Trans*. **1997**, *93* (6), 1065.

(12) Modiano, S. H.; Dresner, J.; Lim, E. C. *Chem. Phys. Lett*. **1992**, *189*, 144.

(13) (a) Mataka, S.; Takahashi, K.; Hirota, T.; Takuma, H.; Kobayashi, M.; Tashiro, M.; Imada, K.; Kuniyoshi, M. *J. Org. Chem*. **1986**, *51*, 4618. (b) Mataka, S.; Mimura, T.; Lee, S. T.; Kobayashi, H.; Takahashi, K.; Tashiro, M. *J. Org. Chem*. **1989**, *54*, 5237.

(14) Agosta, W. C. *J. Am. Chem. Soc*. **1967**, *89*, 3505.

(15) Tung, C.-H.; Wang, Y.-M. *J. Am. Chem. Soc*. **1990**, *112*, 6322.

(16) (a) Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* **1968**, *48*, 2589. (b) Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* **1968**, *49*, 5066.

(17) Saigusa, H.; Sheng, S.; Lim, E. C. *J. Phys. Chem*. **1992**, *96*, 10099.

(18) Katoh, R.; Katoh, E.; Nakashima, N.; Yuuki, M.; Kotani, M. *J. Phys. Chem*. **1997**, *101*, 7725.

(19) Modiano, S.; Dresner, J.; Cai, J.; Wang, X.; Lim, E. C. Unpublished results.

(20) Tero-Kubota, S.; Miyamoto, T.; Akiyama, K.; Ikegami, Y.; Mataka, S.; Tashiro, M. *Chem. Phys. Lett*. **1996**, *249*, 314.

(21) Wang, X.; Lim, E. C., unpublished results.

(22) NIST Standard Reference Database, Number 69—November 1998 Release.